

Systematic tight-binding analysis of ARPES spectra of transition-metal oxides

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We have performed systematic tight-binding (TB) analyses of the angle-resolved photoemission spectroscopy (ARPES) spectra of transition-metal (TM) oxides AMO_3 ($M = Ti, V, Mn$, and Fe) with the perovskite-type structure and compared the obtained parameters with those obtained from configuration-interaction (CI) cluster-model analyses of photoemission spectra. The values of $\epsilon_d - \epsilon_p$ from ARPES are found to be similar to the charge-transfer energy Δ from O $2p$ orbitals to empty TM $3d$ orbitals and much larger than $\Delta - U/2$ (U : on-site Coulomb energy) expected for Mott-Hubbard-type compounds including $SrVO_3$. $\epsilon_d - \epsilon_p$ values from *ab initio* band-structure calculations show similar behaviors to those from ARPES. The values of the $p - d$ transfer integrals to describe the global electronic structure are found to be similar in all the estimates, whereas additional narrowing beyond the TB description occurs in the ARPES spectra of the d band.

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$3d$ transition-metal (TM) oxides have attracted a lot of interest in these decades because of their intriguing physical properties such as metal-insulator transition, colossal magnetoresistance, and the ordering of spin, charge, and orbitals [1]. Photoemission spectroscopy has greatly contributed to the understanding of the electronic structures of these materials. The local electronic structure of strongly correlated $3d$ states of the TM atoms hybridizing with ligand p orbitals has been understood in the framework of the Zaanen-Sawatzky-Allen (ZSA) diagram [2] based on the configuration-interaction (CI) cluster-model analyses of core-level and valence-band angle-integrated photoemission spectra [3, 4, 5]. On the other hand, how the energy band structure of the periodic lattice emerges from the correlated local electronic structure has been an extremely difficult problem as has been extensively discussed in the case of f -electron systems [6, 7], and no clear scenario has been established so far. On the experimental side, rather surprisingly Sarma *et al.* [8] have found that the angle-integrated valence-band photoemission spectra of various perovskite-type $3d$ TM oxides can be well reproduced by band-structure calculation based on the local spin-density approximation in spite of the strong electron correlation.

In order to address the issue of a proper description of the periodic systems with strong correlation, the experimental determination of band dispersions by angle-resolved photoemission spectroscopy (ARPES) has been highly required, but such data have been largely limited to low dimensional compounds [9, 10, 11] of limited chemical variety. For three-dimensional perovskite ox-

ides, which have a wide variety of chemical compositions, even when bulk single crystals are available, they do not have cleavage planes required for ARPES measurements. Recently, technological development has made it possible to grow high-quality single-crystal thin films using the pulsed laser deposition method, and a setup has been developed for their film growth followed by *in-situ* photoemission measurements [12, 13, 14, 15]. Since ARPES data have accumulated for various $3d$ TM oxides of perovskite structures [$SrTiO_3$ (STO) [16], $SrVO_3$ (SVO) [17], $La_{1-x}Sr_xMnO_3$ (LSMO) [18, 19], $Pr_{1-x}Ca_xMnO_3$ (PCMO) [20] and $La_{1-x}Sr_xFeO_3$ (LSFO) [21]] and have been analyzed using a parameterized nearest-neighbor tight-binding (TB) model [22, 23, 24, 25], we are in a position to look at the systematic variation of the electronic structure of the periodic lattice of $3d$ TM atoms and derive empirical rules, as has been done for the local electronic structure by ZSA [2]. In particular, since there is no established theoretical description for correlated periodic systems, it is highly desirable to obtain relationship between parameters in CI theory and those describing ARPES band structures. In this paper, we examine the TB parameters that describe the ARPES band dispersion in order to deduce systematic variations of the energy level (ϵ_d) of TM $3d$ orbitals relative to that (ϵ_p) of O $2p$ orbitals and the $p - d$ transfer integrals [Slater-Koster parameter ($pd\sigma$)] and compare them with those derived from the CI cluster-model analyses of angle-integrated photoemission spectra, namely, ($pd\sigma$), the charge-transfer (CT) energy from the O $2p$ orbitals to the empty TM $3d$ orbitals denoted by Δ , and the aver-

age $3d - 3d$ on-site Coulomb interaction energy denoted by U . For comparison, we have also fitted the *ab initio* band structure to the same TB model, as has been done in Ref. [26]. The values of $\epsilon_d - \epsilon_p$ from ARPES were found to be similar to Δ rather than $\Delta - U/2$ expected for Mott-Hubbard (MH) type compounds. The values of $|(pd\sigma)|$ (determined from the O $2p$ band dispersions) were found to be similar in these estimates, but additional narrowing in the d band (by a factor of $0.3 - 0.5$) was seen in ARPES beyond the TB description.

All the ARPES data analyzed in this paper were measured using a photoemission spectroscopy system combined with a laser molecular beam epitaxy chamber at beamline BL-1C of the Photon Factory, KEK [12]. Details of the experimental conditions for the respective materials were described in Refs. [16, 17, 18, 19, 20, 21]. The *ab initio* band-structure calculations were performed using the linearized augmented plane wave method implemented in the WIEN2K package [27]. The exchange and correlation effects are treated within the generalized gradient approximation [28]. We assumed a cubic paramagnetic (PM) state, and the lattice constants were taken as 3.91\AA for STO, 3.84\AA for SVO, 4.04\AA for LaMnO₃ (LMO), and 4.02\AA for LaFeO₃ (LFO). We fitted the ARPES and *ab initio* results to parameterized nearest-neighbor TB band structures [22, 23, 24, 25]. We assumed the PM state for the ARPES results of STO and SVO, the ferromagnetic (FM) state for LSMO, the C-type antiferromagnetic (AF) state for PCMO, and the G-type AF state for LSFO. The size of the matrix for the calculations were 14×14 (TM $3d$ orbitals: 5, oxygen $2p$ orbitals: $3 \times 3 = 9$) in the cases of PM and FM states, and 28×28 in the cases of AF states. The effects of ferromagnetism and antiferromagnetism were treated phenomenologically by assuming an energy difference ΔE between the spin-up and spin-down TM sites. Parameters to be adjusted are ΔE , the energy level of the TM $3d$ orbitals relative to that of the O $2p$ orbitals, $\epsilon_d - \epsilon_p$, and Slater-Koster parameters $(pd\sigma)$, $(pd\pi)$, $(pp\sigma)$, and $(pp\pi)$ [29]. In the cases of the FM and AF states, ϵ_d is the average of the up-spin d level $\epsilon_d - \Delta E/2$ and the down-spin d level $\epsilon_d + \Delta E/2$. The details of the matrix elements for the calculations were described in Refs. [23, 25].

In the CI cluster-model calculations [3, 4, 5, 30], a TMO₆ octahedral cluster is considered. In this model, the ground state is described as

$$\Psi_g = \alpha_1|d^n\rangle + \alpha_2|d^{n+1}\underline{L}\rangle + \alpha_3|d^{n+2}\underline{L}^2\rangle + \dots$$

The final state for the emission of a TM $2p$ core electron is given by

$$\Psi_f = \beta_1|\underline{c}d^n\rangle + \beta_2|\underline{c}d^{n+1}\underline{L}\rangle + \beta_3|\underline{c}d^{n+2}\underline{L}^2\rangle + \dots$$

where \underline{c} denotes a TM $2p$ core hole. The final state for the emission of a TM $3d$ electron is given by

$$\Psi_f = \gamma_1|d^{n-1}\rangle + \gamma_2|d^n\underline{L}\rangle + \gamma_3|d^{n+1}\underline{L}^2\rangle + \dots$$

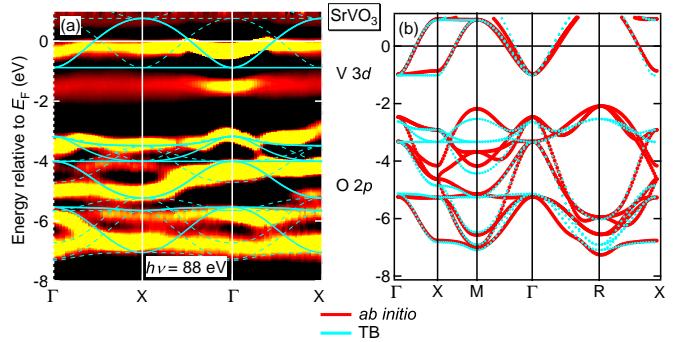


FIG. 1: (Color online) Tight-binding fit to the ARPES spectra [17] (a) and *ab initio* band-structure calculation (b) for SrVO₃. In panel (a), bright parts correspond to energy bands.

In this work, we have taken the parameter values of STO and SVO from Ref. [30], and those for LSMO and LSFO from Refs. [31, 32], where these values have been obtained by fitting the TM $2p$ core-level and valence-band photoemission spectra.

In Fig. 1, we show an example of the TB fit to the ARPES spectra and *ab initio* band-structure calculation. Figure 1 (a) shows a fit to the ARPES spectra of SVO [17]. The bands below ~ -3 eV are mainly from O $2p$ states, and those between ~ -2 eV and E_F are mainly from V $3d$ states. The dispersions of the O $2p$ bands were well reproduced by the calculation, but the widths of the V $3d$ bands were about 50% of the calculated ones. Such a mass renormalization is also observed in the ARPES spectra of LSMO [18] and high- T_C cuprates [9]. Figure 1 (b) shows a TB fit to the *ab initio* band-structure calculation of SVO. The parameters $\epsilon_d - \epsilon_p = 3.6$ eV and $(pd\sigma) = -2.2$ eV give a fairly good fit to the *ab initio* calculation.

Figure 2 shows comparison of the variation of $|(pd\sigma)|$ [panel (a)] and $\epsilon_d - \epsilon_p$ [panel (b)] for ARPES and *ab initio* compared with parameter values deduced from CI cluster-model analysis. As seen from Fig. 2 (a), the values of $(pd\sigma)$ are similar in all the three estimates. This means that, as far as the strength of $p - d$ hybridization is concerned, the values from the local CI cluster-model analysis can be used to describe the band structures of periodic systems. The behavior of $\epsilon_d - \epsilon_p$ from ARPES follows Δ from CI analysis, as shown in Fig. 2 (b). The $\epsilon_d - \epsilon_p$ values from *ab initio* calculations are similar to or a little (by ~ 1 eV) smaller than those from ARPES. This reflects the well-known tendency of *ab initio* calculations to underestimate the band gaps and the binding energies of the O $2p$ bands. One typical example is the underestimation of the values of the bad gaps in STO [33]. The indirect ($R \rightarrow \Gamma$) and direct ($\Gamma \rightarrow \Gamma$) gaps are calculated to be 1.9 eV and 2.2 eV, while the experimental values are 3.25 eV and 3.75 eV. However, as this difference is

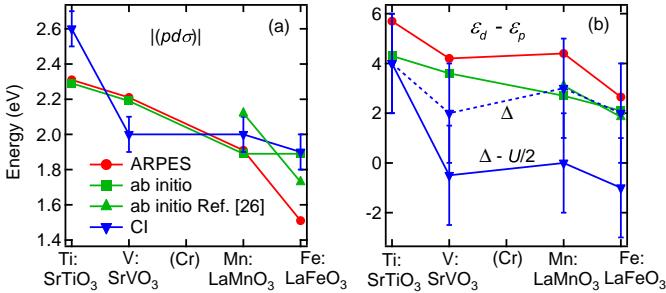


FIG. 2: (Color online) Material dependences of the $p-d$ transfer integral ($|(|pd\sigma|)|$) (a) and the energy level of TM d relative to O $2p$ ($\epsilon_d - \epsilon_p$) (b) deduced from ARPES and *ab initio* calculations compared with those from CI calculation. Values from *ab initio* calculations in Ref. [26] has been also plotted. The CI parameter values of STO and SVO are taken from Ref. [30], and those for LSMO and LSFO are from Refs. [31, 32].

rather small, one may conclude that *ab initio* calculations can describe the angle-integrated photoemission spectra of these materials fairly well [8]. It is remarkable to see that, except for the common shift of the O $2p$ band, the experimental $\epsilon_d - \epsilon_p$ of complicated origin is well reproduced by the simple *ab initio* calculation.

For the d^0 compound (STO), the value of $\epsilon_d - \epsilon_p$ is expected to be given by Δ . In the case of MH-type compounds such as SVO, $\epsilon_d - \epsilon_p$ is expected to be given by $\Delta - U/2$ [26]. However, Fig. 2 shows that the $\epsilon_d - \epsilon_p$ values from ARPES are closer to Δ than $\Delta - U/2$ for all compounds including SVO. One should note here that the values of Δ shows strong dependence on TM atoms and changes from ~ 0 to ~ 6 eV, whereas those of U do not strongly depend on TM atoms and are as large as $5 - 8$ eV [3, 30].

To understand the difference in $\epsilon_d - \epsilon_p$ between ARPES and the simple MH picture even for SVO, we consider the single-particle energy diagrams for MH type compounds, where $\Delta > U$, [panel (a)] and CT type compounds, where $\Delta < U$, [panel (b)] and the assignments of band characters as shown in Fig. 3. In a MH-type compound, the TM $3d$ states are located above the O $2p$ band, and the $p-d$ hybridization simply causes upward and downward shifts of the p and d levels, respectively, leading to little difference between ARPES and CI. Therefore, in pure MH-type compounds, the relationship $\epsilon_d - \epsilon_p = \Delta - U/2$ holds, which is inconsistent with our results. In a CT-type compound, the effect of $p-d$ hybridization is complicated, creating new states in the occupied part, i.e., in the electron removal spectrum. That is, a charge-transfer satellite of d^{n-1} final-state character appears below the O $2p$ band and the split-off state of the Zhang-Rice (ZR) states ($d^n \underline{L}$ final-state character) are formed above the O $2p$ band as a result of $p-d$ hybridization, as shown in Fig. 3 (b). In the case of a d^9 system (Cu^{2+}), the ZR

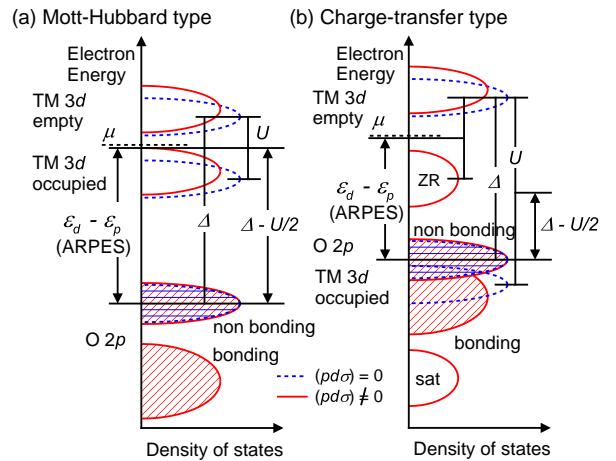


FIG. 3: (Color online) Energy diagrams for Mott-Hubbard-type (a) and charge-transfer-type (b) compounds. Sat: charge-transfer satellite (d^n); ZR: Zhang-Rice singlet-like states ($d^n \underline{L}$). Here, $\epsilon_d - \epsilon_p$ is the $3d$ level relative to O $2p$, Δ is the charge-transfer energy from O $2p$ to the empty TM $3d$, and U is the $3d - 3d$ on-site Coulomb interaction energy.

state becomes a spin singlet, well known as the ZR singlet [34]. The emergence of the charge-transfer satellite and the ZR state can be understood from the Anderson impurity model, where the discrete TM $3d$ impurity states interact with the O $2p$ continuum states through strong $p-d$ hybridization and two new split-off states are created. When we fit the ARPES results, we consider the ZR state as “effective” TM $3d$ bands. This explains why the $\epsilon_d - \epsilon_p$ values in ARPES becomes considerably larger than $\Delta - U/2$ in the CT-type compounds as shown in Fig. 3(b). The difference of these two is large also in SVO, which has long been considered as a typical MH compound. This result shows that SVO is not a pure MH compound and hybridization between O $2p$ and V $3d$ states is comparable to CT-type compounds, as already suggested in Fig. 15 in Ref. [30] and concluded by the recent CI calculation in Ref. [35].

The similarity of the $\epsilon_d - \epsilon_p$ values in *ab initio* and ARPES shows that in *ab initio* $\epsilon_d - \epsilon_p$ is similar to Δ not to $\Delta - U/2$. This result means that the d bands in *ab initio* calculations are not the pure d bands before $p-d$ hybridization but the ZR state after being considerably hybridized with O $2p$ states.

Finally, we would like to comment the limitation of our analyses of the ARPES spectra. The values of $|(|pd\sigma|)|$, which describes the global electronic structure, were similar in the cases of ARPES, *ab initio*, and CI, but the d -band narrowing observed in ARPES were about 1/2 or 1/3, which cannot be described in the TB band-structure

calculation. This is the effect of electron correlation at the TM sites.

In conclusion, we have compared the parameters obtained from TB fit to the ARPES spectra of TM oxides AMO_3 ($M = Ti, V, Mn$, and Fe) and those obtained by TB fit to the *ab initio* band-structure calculation with those from CI cluster-model calculations. The $\epsilon_d - \epsilon_p$ values obtained by TB fit to *ab initio* band-structure calculations were a little smaller than those in ARPES, reflecting the general tendency of *ab initio* calculations to underestimate the binding energies of O 2p bands. The $\epsilon_d - \epsilon_p$ values from ARPES were significantly larger than $\Delta - U/2$ for all the compounds including SVO, which has been considered as a typical MH system. We attribute this trend to the ZR-band origin of the effective *d* band. The values of $|(pd\sigma)|$ were found to be similar in all the three estimates, showing the validity of using parameters obtained from the local cluster or impurity Anderson models to describe the global electronic band structure of the TM oxides. However, the narrowing of the (“effective”) *d* band seen in ARPES was beyond the TB description.

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